

# PATENT ABSTRACTS OF JAPAN

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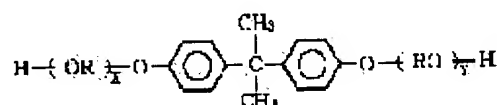
(22)Date of filing : 02.10.1992 (72)Inventor : KUBO SHINJI  
TAJIRI TAKAYUKI  
IWASAKI HITOSHI  
NAGAI YOICHI

## (54) POLYESTER RESIN FOR TONER

### (57)Abstract:

PURPOSE: To provide a polyester resin for a toner having satisfactory melt flowability and fixability at a low temp. and excellent in blocking resistance.

CONSTITUTION: This polyester resin for a toner consists of acid components including  $\geq 50\text{mol}\%$  terephthalic acid and/or isophthalic acid and diol components including  $5\text{-}80\text{mol}\%$  diol represented by formula and hydrogenated bisphenol A based on the amt. of all the acid components and has  $\leq 115^\circ\text{C}$  softening temp. and  $\geq 60^\circ\text{C}$  glass transition temp. In the formula, R is  $\leq 3\text{C}$  alkylene, each of X and Y is an integer of  $\geq 0$  and  $2 \leq X+Y \leq 7$ .



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## DETAILED DESCRIPTION

### [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to polyester resin useful as a dry type toner used for the development of an electrostatic-charge image or a magnetic latent image in a xerography, an electrostatic recording method, electrostatic print processes, etc. In more detail, it excels in a blocking resistance, a melting fluidity, and low-temperature fixing nature, and is related with the polyester resin for toners useful as the high-speed copying machine with which the object for full color as which a high melting fluidity is required especially, and low-temperature fixing nature are demanded, and an object for high speed printers.

[0002]

[Description of the Prior Art] In the method of obtaining \*\*\*\* more lasting than an electrostatic-charge image, it is established, after developing negatives with the toner which electrified beforehand the electrostatic-charge image formed on the photoconductivity photo conductor or the electrostatic recording object by friction. In the case of a magnetic latent image, it is established after developing the latent image on a magnetic drum with the toner containing the magnetic substance. After fixing makes the toner image obtained by development weld directly on a photoconductivity photo conductor or an electrostatic recording object or imprints a toner image on paper or a film, it is performed by making this weld on an imprint sheet. Although weld of a toner image is performed by contact with a solvent steam, pressurization, or heating and there are a non-contacted heating method in electric oven and a sticking-by-pressure heating method with a pressurization roller as heating method, recently when improvement in the speed of a fixing process is demanded, the latter is mainly used.

[0003] There are 1 component system toner and a two-component system toner as toner used by the dry-developing method. after the two-component system toner's having carried out melting kneading of a resin, a coloring agent, an electric charge control agent, and the required additive and making it fully distribute them first in addition to this -- subsequently -- coarse grinding -- it pulverizes, and is classified and manufactured by the predetermined size range 1 component system toner adds the magnetic iron powder other than each component of the toner of the above-mentioned two-component system, and is manufactured similarly.

[0004] Since a resin is a principal component under toner combination, it governs most performances required of a toner. For this reason, it is required for the resin for toners that the dispersibility of the coloring agent in the melting kneading process in toner manufacture and the grindability in a pulverization process should be good etc., and various performances -- fixing nature, offset nature, blocking nature, and an electrical property are good -- are required of it in use of a toner. As a resin used for manufacture of a toner, although an epoxy resin, polyester resin, polystyrene resin, an methacrylic system resin, etc. are well-known, as for the object for sticking-by-pressure heating fixing methods, styrene and the copolymer of an acrylic ester (meta) have mainly been used. However, since the low-temperature fixing nature of a toner is strongly demanded in connection with the high speed inclination of a copying machine, when the vinyl chloride-proof plasticizer nature of a toner image it can be

established more at low temperature and to which it was fixed are excellent, polyester resin attracts attention.

[0005] Furthermore, you have to color making the toner of three to 4 color adhere to a transfer paper in an above-mentioned development process, and carrying out melting mixture in a fixing process subsequently, in order to obtain a color picture, and have to make it established. the binder for full color toners -- a resin with the miscibility sufficient as mentioned above in a fixing process -- if it puts in another way, a good resin of a melting fluidity is desired strongly When the good binder of a melting fluidity is used, there is a problem which the offset phenomenon-proof in a fixing process produces. However, if a binder is made to construct a bridge or it macromolecule-izes, in order to prevent an offset phenomenon, since a melting fluidity will fall, as a resin for binders for full color toners, it is not suitable. Therefore, the silicone oil etc. is applied to a fixing roller front face in order to obtain un-offsetting nature in the case of the copying machine for full color.

[0006] Moreover, there are not few examples for which the technique of offset prevention, such as applying a silicone oil etc. to a fixing roller, is used also in the common copying machine except full color and the printer today when improvement in the speed of the fixing section and energy saving are desired strongly.

[0007]

[Problem(s) to be Solved by the Invention] The binder resin for the object for full color toners or the toner for high-speed copying machines has the need for hypoviscosity-izing (reduction in a softening temperature) for melting mixture or low energy melting. The more it generally hypoviscosity-izes polymer, a glass transition temperature (T<sub>g</sub>) becomes low and, the more a blocking resistance falls.

[0008] In full color development, by high definition, the high binder of thermal stability has the as much as possible useful resin of high T<sub>g</sub> as much as possible at hypoviscosity, and the resin to which hypoviscosity and quantity T<sub>g</sub>-ization progressed is demanded.

[0009] The purpose of this invention has a melting fluidity and good low-temperature fixing nature, and they are to offer the resin for toners excellent in the blocking resistance.

[0010]

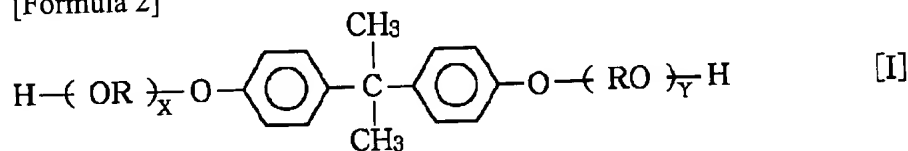
[Means for Solving the Problem] In order to solve these problems, when this invention persons inquired wholeheartedly and hydrogenation bisphenol A was used, they found out that hypoviscosity and quantity T<sub>g</sub>-ization were promoted.

[0011] Moreover, this invention persons found out that further hypoviscosity and quantity T<sub>g</sub>-ization could be attained by using hydrogenation bisphenol A together for the diol component expressed with a formula [I], although the diol expressed with a formula [I] had found out promoting hypoviscosity and quantity T<sub>g</sub>-ization previously.

[0012] namely, this invention -- a terephthalic acid and/or an isophthalic-acid component -- more than 50 mol % -- it is polyester resin for toners characterized by being polyester which condensed the diol and hydrogenation bisphenol A which are expressed in a formula (I) as the included acid component to all acid components from % of the 5 - 80-mol included diol which comes out of comparatively, for the softening temperature (T<sub>1</sub>) of this polyester being 115 degrees C or less, and a glass transition temperature (T<sub>2</sub>) being 60 degrees C or more

[0013]

[Formula 2]



(R expresses a three or less-carbon number alkylene machine among a formula, and x and y are zero or more each [ which fills 2 ≤ x+y ≤ 7 ] integers.)

[0014]

[Function] The terephthalic acid and/or isophthalic-acid component as used in the field of this invention

mean more than a kind chosen from the group which consists of a terephthalic acid, isophthalic acids, and those low-grade alkyl ester. These aromatic dicarboxylic-acid components have the effect which raises Tg of polyester resin, and raise the blocking resistance of a toner. for this reason, a terephthalic acid and/or an isophthalic-acid component -- all the inside of an acid component -- more than 50 mol % -- it is necessary to use it -- more than 60 mol % -- it is desirable to use it

[0015] As an example of the acid component of others which can be used by this invention, these acid anhydrides, such as a phthalic acid, a sebacic acid, an isodecyl succinic acid, a maleic acid, a fumaric acid, adipic acids and these monomethyl, monoethyl, a dimethyl, and diethyl ester, are mentioned. These dicarboxylic-acid components affect the fixing nature and the blocking resistance of a toner greatly. It can be used in the range which does not exceed 50-mol % according to the military requirement of a resin.

[0016] In this invention, it is required to use the diol expressed with a formula [I] as a diol component and hydrogenation bisphenol A. These diols component has the effect of maintaining a softening temperature comparatively low, and can improve [ consequently ] the melting fluidity of a toner, and a blocking resistance while it raises Tg of polyester resin. And this effect is heightened more by using hydrogenation bisphenol A with the diol expressed with a formula [I].

[0017] The total quantity of the diol expressed with the formula in polyester resin [I] and hydrogenation bisphenol A needs to be 5 - 80-mol % to all acid components. if the effect that the diol expressed with a formula [I] and hydrogenation bisphenol A raise Tg has bad high bur reactivity and those total quantities exceed 80-mol %, until predetermined Tg will be obtained -- \*\*\*\* -- polymerization degree does not go up Moreover, it is a book when those total quantities are less than [ 5 mol % ]. Moreover, hydrogenation bisphenol A is expensive and the thing using this is not so much suitable for use to the copying machine and printer which has generally spread. Moreover, in order that the diol and hydrogenation bisphenol A which are expressed with a formula [I] may tend to cause a pyrolysis at an elevated temperature, the amount used is restricted to the combined use with the aromatic dicarboxylic acid which needs hot polymerization temperature. This inclination is large in especially hydrogenation bisphenol A. In addition, the amount of the diol as used in the field of this invention means not the charge in a polycondensation reaction but the amount which converted into the diol the diol unit which constitutes polyester resin.

[0018] As the example of a diol expressed with a formula [I] Polyoxyethylene - (2.0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (2.0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene (2.2)-polyoxyethylene - (2.0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene-(6)-2 and 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (2.2) -2, 2-screw (4-hydroxyphenyl) propane, polyoxypropylene-(2.4)-2 and 2-screw (4-hydroxyphenyl) propane, polyoxypropylene (3.3) -2, 2-screw (4-hydroxyphenyl) propane, etc. are mentioned, and these are independent -- or it is mixed and used Polyoxyethylene-(n)-2 and 2-screw (4-hydroxyphenyl) propane which are polyoxypropylene-(n)-2 which are  $2.1 \leq n \leq 2.5$ , 2-screw (4-hydroxyphenyl) propane, and  $2.0 \leq n \leq 3.0$  is especially desirable.

[0019] As for the residue of the diol used by this invention, it is desirable that it is an aliphatic diol. as an example of an aliphatic diol, ethylene glycol, neopentyl glycol, a propylene glycol, butanediol, a polyethylene glycol, etc. are mentioned, and these are independent -- or it is mixed and used These aliphatic diols have the operation which raises a condensation polymerization reaction rate. Ethylene glycol, neopentyl glycol, and butanediol are desirable from the point of fixing nature also in these.

[0020] In addition, unless oxy acid, such as a p-oxy-benzoic acid, p-oxymethyl benzoic acid, and a p-oxy-ethyl benzoic acid, also spoils the military requirement of the polyester resin of the resin of this invention, it can be used in the range which does not exceed ten-mol % to all acid components.

[0021] In this invention, the most important point is that the softening temperature (T1) of the polyester resin obtained from the above-mentioned acid component and a diol by carrying out condensation polymerization is 115 degrees C or less, and Tg (T2) is 60 degrees C or more.

[0022] When the softening temperature exceeded 115 degrees C and it is used as a binder for full color, melting miscibility falls and a high picture is not acquired. Therefore, though there was a problem of a

grade, when the glossiness of the miscibility and the duplication of a color is considered, a softening temperature at least has the need 115 degrees C or less. Moreover, if full color, in order to raise the resolution of a duplication, the particle size of a toner is turning minutely in recent years, and it is easy to generate blocking on the level of the conventional resin for toners as the surface area is large. Moreover, since the process of mixture of a color increases as compared with full color \*\* and a common copying machine, copy stability is further needed. If a toner is ground in a copy process or it welds except the fixing section, it will lead to a direct picture fall. Therefore, in order to acquire a high picture by high storage stability, Tg needs to be 60 degrees C or more.

[0023] The inclination for a correlation to have the relation between a softening temperature and Tg to some extent in the same resin system, and for a softening temperature to become high about a resin with high Tg is remarkable. A binder resin which fills high Tg with a low softening temperature simultaneously is an outstanding resin, and is the binder which was as excellent in full color toners as what has the small difference (T1-T2) of a softening temperature (T1) and Tg (T2). In order to fill both melting mixture and storage stability simultaneously, the difference (T1-T2) of a softening temperature (T1) and Tg (T2) has desirable less than 50 degrees C.

[0024] the polyester resin of this invention teaching the aforementioned monomer to a reaction iron pot, and carrying out a heating temperature up -- an esterification reaction -- or an ester exchange reaction is carried out and it is manufactured. The esterification catalyst used if needed by a usual esterification reaction or usual ester exchange reactions, such as a sulfuric acid, titanium butoxide, dibutyltin oxide, a magnesium acetate, and manganese acetate, at this time can be used. Subsequently, water and alcohol which were produced at the reaction according to the conventional method are removed. Although polymerization reaction is advanced succeedingly, it is desirable to perform a polymerization, carrying out distillate removal of the diol component under the vacuum of 150 or less mmHg at this time.

[0025] Thus, in order to manufacture a toner using the obtained polyester resin, there is especially no limitation that what is necessary is just to follow a well-known method conventionally. For example, by carrying out the amount combination of requests and kneading additives various for the purpose, such as coloring and electric charge control, the constituent for toners can be prepared and a toner can be obtained by pulverizing it etc. As an additive, the metal complex of carbon black, iron black, graphite, a Nigrosine, and a monoazo color, ultramarine blue, a copper phthalocyanine blue, Hansa yellow, a benzidine yellow, cinchona bark KUDOKU drine compounds, various lake pigments, etc. are mentioned, for example. Moreover, on the occasion of manufacture of a toner, it is a book besides the polyester resin by this invention. As this polymer, silicone resin, polyurethane, a polyamide, an epoxy resin, conversion rosin, a terpene resin, phenol resin, aliphatic series or an alicycle group hydrocarbon resin, an aromatic system petroleum resin, chlorinated paraffin, paraffin wax, etc. are mentioned. Moreover, mean particle diameters, such as metal; magnetites, such as iron, manganese, nickel, cobalt, and chromium, a hematite, various ferrites, a manganese alloy, and other ferromagnetic alloys, can also include an about 0.05-5 micrometers (preferably 0.1-2 micrometers) magnetic particle in a toner. the content -- usually -- 15- of toner AUW -- it is 25 - 45 % of the weight preferably 70% of the weight. Moreover, you may make a toner contain flow improvers, such as hydrophobic colloidal silica, ten to 40% of the weight. Of course, this flow improver may be mixed and used for the exterior of a resin constituent, and is about 0.5 - 5 % of the weight as an addition. this invention -- setting -- a softening temperature -- the Shimadzu Corp. make -- the time of measuring using flow-tester CFT-500 under 1mm phix10mm a nozzle, load 30kf, 3 degrees C of programming rates, and the uniform temperature up of min -- sample 1.0g -- inner one half -- an outflow -- it defines as temperature the bottom. Moreover, Tg is defined using a differential \*\*\*\* calorimeter as temperature of the intersection of the base line of the chart when measuring by 5 degrees C of programming rates, and min, and the tangent of the endothermic curve near the Tg.

[0026] Moreover, the component analysis in an example understood the resin an added water part by the hydrazine, and it carried out the fixed quantity by liquid chromatography.

[0027]

[Example] Next, this invention is not limited by this although an example explains this invention.

An example 1, the example 1 of comparison - the 100 mol section of 2 terephthalic acids, -2 and 30 mol (it is hereafter called Diol A for short) section of polyoxypropylene-(2.3) 2-screw (hydroxyphenyl) propanes, the 30 mol section of hydrogenation bisphenol A, and the 70 mol section of ethylene glycol were supplied to the reaction container which has a distilling column. The condensation reaction was performed decompressing to 1.0mmHg(s) over 30 minutes, maintaining at 200 degree C of inside \*\*, and making ethylene glycol distill, after having added the antimony trioxide which is a catalyst 0.05% of the weight to all acid components, maintaining inside \*\* at 260 degrees C and churning rotational frequency 120rpm and carrying out an esterification reaction under an ordinary pressure. The terminal point of a condensation reaction was set up in 1 and 2 or 3 hours, and three sorts of resins R-1 to R-3 were obtained.

[0028] The component analysis (unit : mole ratio) of R-1 to R-3 and the softening temperature, and the measurement result of Tg were shown in Table 1.

[0029]

[Table 1]

表 1

	R-1	R-2	R-3
テレフタル酸 (モル比)	100	100	100
ジオールA (モル比)	30.0	30.2	30.3
水素添加ビスフェノールA	28.3	28.0	27.8
エチレングリコール	51.0	50.9	50.6
軟化温度T <sub>1</sub> (°C)	97	104	120
ガラス転移温度T <sub>2</sub> (°C)	55.4	61.8	76.6
T <sub>1</sub> - T <sub>2</sub> (°C)	41.6	42.2	43.4

Since Tg was also over 60 degrees C by the low softening temperature, when it used as a resin for full color toners, also as for the melting fluidity, R-2 (example 1) was good, and excellent also in storage stability.

[0030] R-1 (example 1 of comparison) had the softening temperature as low as 101 degrees C because of low polymerization degree, and although the melting fluidity was very good, Tg of storage stability was low for the 55.4-degree-C and low reason. Moreover, for low Tg, the development toner within a copying machine deteriorated, or it welded to development in process and the machine, and was not suitable for the particle full color toner which pursues high definition.

[0031] R-3 (example 2 of comparison) -- R- although it was 1 or 2 high-polymer articles, Tg was very as high as 76.6 degrees C, and although storage stability was excellent, since the softening temperature was as high as 120 degrees C, it was not suitable for the binder for full color toners with which the melting fluidity is pursuing high definition

[0032] these results showed that the physical properties as a resin for toners changed greatly with differences in polymerization degree, even when preparation composition was the same

Except having made brewing composition of an example 2, the example 3 of comparison - 4 diol components into the diol A 100-mol section, the 20 mol section of hydrogenation bisphenol A, and the 60 mol section of ethylene glycol, by the example 1 and this operation, the terminal point of a condensation reaction was set up in 5 and 6 or 7 hours, and R-4 to R-6 was obtained for three sorts of

resins. The component-analysis result (mole ratio) of R-4 to R-6 and the measurement result of a physical-properties value were shown in Table 2.

[0033]

[Table 2]

表 2

	R-4	R-5	R-6
テレフタル酸 (モル比)	100	100	100
ジオールA	50.6	50.6	50.3
水素添加ビスフェノールA	20.0	18.9	18.5
エチレングリコール	31.5	31.3	30.6
軟化温度 $T_1$ (°C)	95	99	101
ガラス転移温度 $T_2$ (°C)	50.2	57.6	61.0
$T_1 - T_2$ (°C)	44.8	42.4	40.0

R-6 (example 2) of polymerization temperature 7 hours is a low softening temperature (101 degrees C) and the resin which maintained very much balance with high Tg (61 degrees C), and excelled Table 2 also in the melting fluidity as full color, the storage stability as a particle toner, and print durability.

[0034] On the other hand, although R-4 (example 3 of comparison) and R-5 (example 4 of comparison) were hypoviscosity, polymerization degree was insufficient and Tg did not amount to 60 degrees C. Therefore, although it was possible to use of a common copying machine, for using it for the particle full color toner which aimed at high resolution, Tg was low. Moreover, although the melting fluidity was good, storage stability and \*\*\*\*\*-proof were missing.

Except having changed the example 5 of comparison - 7 brewing composition, as shown in Table 3, the same operation as an example 1 was performed, the terminal point of a condensation reaction was set up in 2 and 3 or 1 hour, respectively, and R-7 to R-9 was obtained for three sorts of resins. The component-analysis result (mole ratio) of R-7 to R-9 and the measurement result of a physical-properties value were shown in Table 3.

[0035]

[Table 3]



表 3

	R-7	R-8	R-9
テレフタル酸	30	100	50
イソフタル酸	10		50
アジピン酸	60		
ジオールA	30	50	
水素添加ビスフェノールA	30		
ネオペンチルグリコール			50
エチレングリコール	70	80	80

(単位：モル部)

From Table 3, although R-7 (example 5 of comparison) was a case with little amount of the aromatic dicarboxylic acid used of an acid component, it was understood that Tg is comparatively low with a high softening temperature. When not using hydrogenation bisphenol A and Diol A of R-9 (example 7 of comparison), similarly, the softening temperature was high and Tg was low. Therefore, when these resins were used for full color toners, the margin fluidity was also inadequate and storage stability was also low.

[0036] Also by these results, it turns out that an aromatic dicarboxylic acid and hydrogenation bisphenol A promote high Tg-ization by hypoviscosity.

[0037] Moreover, when hydrogenation bisphenol A was used together, the inclination of hypoviscosity and a raise in Tg was inferior, although a certain amount of hypoviscosity-ization was attained also of the bisphenol A component like R-8 (example 6 of comparison) when a hydrogenation bisphenol A component was not used.

[0038]

[Table 4]

表 4

	R-7	R-8	R-9
テレフタル酸	29.9	100	49.8
イソフタル酸	10.1		50.2
アジピン酸	60.0		
ジオールA	30.2	50.2	
水素添加ビスフェノールA	28.3		
ネオペンチルグリコール			50.3
エチレングリコール	42.2	50.9	50.5
軟化温度 $T_1$ (°C)	115	106	115
ガラス転移温度 $T_2$ (°C)	48.2	55.8	52.8
$T_1 - T_2$ (°C)	66.8	50.2	62.2

[0039]

[Effect of the Invention] Since the resin for toners of this invention is a low softening temperature in spite of being high  $T_g$ , it is excellent as a resin for toners for the object for full color, or high-speed copying machines, and it was excellent also in storage stability.

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[Translation done.]